

those references demonstrates the meaning of "monolayer," as would have been understood by one of ordinary skill in the art at the time the present application was filed. The Examiner is urged to consider the transmitted material, and to find that the references cited against the pending claims do not disclose, teach, or suggest a "monolayer," as that term would be understood by one of ordinary skill in the art.

Although Jenekhe discloses an embodiment having a "single layer of conductive polymer film" (col. 49, lines 17-19, and Fig. 8), there is no disclosure or suggestion in Jenekhe of a monolayer, as required by the present claims.

As previously noted, Traynor discloses a tractable powder, which is intrinsically and fundamentally distinguishable from a monolayer. Thus, Traynor does not disclose, suggest or teach a monolayer.

Since neither cited reference, alone or in combination, discloses a monolayer, suggests the formation of a monolayer, teaches how to construct a monolayer, or provides motivation for one of ordinary skill in the art to modify either reference to include a monolayer, and since the suggested combination would lack an element of the pending claims, there can be no *prima facie* case of obviousness. Applicants respectfully request reconsideration and withdrawal of the rejections.

The Examiner was kind enough to grant the undersigned a telephone interview on November 14, 2001, in which he indicated that he had received the enclosed references presenting the ordinary meaning of "monolayer," and that he agreed that the cited references did not disclose that which would be understood as a monolayer. However, the Examiner further asserted that other references could be cited which would present further hurdles to the patentability of the present invention. The Examiner also indicated that the finality of the present rejection would be withdrawn, in the interest of presenting such references. Applicants respectfully request that the finality of the pending rejection be withdrawn, and any further references deemed to anticipate or make obvious the present invention be presented.

CONCLUSION

Applicants respectfully submit that the claims are allowable as they stand. Although no fees are believed to be due, please apply any other charges or credits to Deposit Account No. 06-1050, with reference to Attorney Docket No. 02893-036001.

Respectfully submitted,

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An
Introduction to
ULTRATHIN
ORGANIC FILMS
From
Langmuir-Blodgett to Self-Assembly

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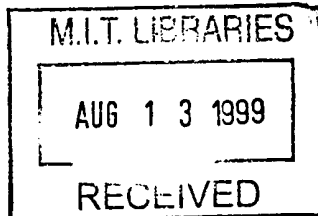
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"Today...I propose to tell you of a real two-dimensional world in which phenomena occur that are analogous to those described in 'Flatland.' I plan to tell you about the behavior of molecules and atoms that are held at the surface of solids and liquids."

— I. Langmuir, *Science* 1936, 84, 379.

PART THREE

SELF-ASSEMBLED MONOLAYERS

Self-assembled (SA) monolayers are molecular assemblies that are formed *spontaneously* by the immersion of an appropriate substrate into a solution of an active surfactant in an organic solvent [1, 2]. There are several types of SA methods that yield organic monolayers. These include organosilicon on hydroxylated surfaces (SiO_2 on Si, Al_2O_3 on Al, glass, etc.) [3–15]; alkanethiols on gold [16–24]; silver [25]; and copper [26–28]; dialkyl sulfides on gold [29]; dialkyl disulfides on gold [30]; alcohols and amines on platinum [29]; and carboxylic acids on aluminum oxide [231–33] and silver [34].

From the energetics point of view, a self-assembling surfactant molecule can be divided into three parts (Figure 3.1). The first part is the head group that provides the most exothermic process, i.e., chemisorption on the substrate surface. The very strong molecular–substrate interactions result in an apparent pinning of the head group to a specific site on the surface through a chemical bond. This can be a covalent Si–O bond in the case of alkyltrichlorosilanes on hydroxylated surfaces; a covalent, but slightly polar, Au–S bond in the case of alkanethiols on gold; or an ionic CO_2^-Ag^+ bond in the case of carboxylic acids on AgO/Ag. The energies associated with the chemisorption are at the order of tens of kcal/mol (e.g., ~40–45 kcal/mol for thiolate on gold [35, 36]). As a result of the exothermic head group–substrate interactions, molecules try to occupy every available binding site on the surface, and in this process they push together molecules that have already adsorbed.

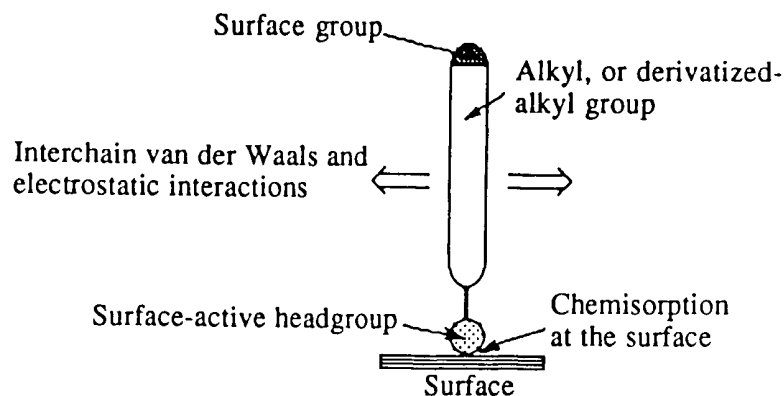


Figure 3.1. A schematic view of the forces in a self-assembled monolayer.

This implies that we assume some surface mobility prior to final pinning, otherwise we cannot explain the formation of crystalline molecular assemblies. The chemisorption exothermicity may be compared, in principle, to the pressure that the barrier in a Langmuir trough applies to the amphiphilic molecules at the water-air interface. It is this spontaneous molecular adsorption that brings molecules close enough together and allows for the short-range, dispersive, London-type, van der Waals forces to become important.

The second molecular part is the alkyl chain, and the energies associated with its interchain van der Waals interactions are at the order of few (<10) kcal/mol (exothermic). It is clear that self-assembly of amphiphilic hydrocarbon molecules cannot be possible given only the interactions among the alkyl chains, and the reader should bear in mind that *the first and most important process is chemisorption*. Only after molecules are put in place on the surface can formation of an ordered and closely packed assembly start. Van der Waals interactions are the main forces in the case of simple alkyl chains (C_nH_{2n+1}). On the other hand, when a polar bulky group is substituted into the alkyl chain (Section 4.2.B), there also are long-range electrostatic interactions that, in some cases, are energetically more important than the van der Waals attractions.

The third molecular part is the terminal functionality, which, in the case of a simple alkyl chain, is a methyl (CH_3) group. These surface groups are thermally disordered at room temperature, as is apparent from helium diffraction [26] and FTIR studies [37] in the case of methyl-terminated monolayers, and from surface reorganization studies in the case of hydroxy-terminated monolayers [38]. The energies associated with this process are at the order of a few kTs, where k is the

Bolznmann constant, and T is the absolute temperature. Usually, a value of ~ 0.7 kcal/mol is assigned to every *gauche* bond. (*Trans-gauche* isomerization is an endothermic process.)

We note that the terms *order* and *close-packing* used here are relative and depend upon the point of reference. Usually, we use the term *order* to describe molecular assemblies with translational symmetry, i.e., a two-dimensional crystalline-like monolayer. The term *close-packing* usually is associated with the density of crystalline polyethylene. However, a solid-state physicist who compares SA monolayers to inorganic crystals will conclude that these are *highly disordered* systems because of the number of defects. On the other hand, one who compares SA monolayers to polymer glasses or liquid paraffin would suggest that these are *highly ordered* systems. I feel that from the chemistry point of view, and especially when taking into account electron diffraction and FTIR studies, SA monolayers can be considered ordered, closely packed molecular assemblies. This does not mean that SA monolayers are pinhole- and defect-free. We have discussed in Section 2.3.A the structure of LB monolayers at the water-air interface, and the molecular aggregation even at a very low (as low as zero) surface pressure. Similar aggregation of surfactant molecules can occur, in principle, at the solution-substrate interface, prior to or parallel to chemisorption, which would lead to a Swiss-cheese-like structure. We mentioned this possibility in Section 1.1.A in the discussion on ellipsometry. We note, again, that structures containing defects that are larger than very few molecular diameters cannot be stable. Such structures should collapse to either completely disordered, glass-like systems, or to systems where ordered molecular assemblies are embedded in a bulk of a glassy material, depending on chain length. A recent work by Evans *et al.* may provide some support for this suggestion. Their study indicated that OH surfaces (in alkanethiol monolayers on gold) reorganize with kinetics that is strongly dependent on chain length [38]. They suggested that the reorganization process may start from pinholes and grain boundaries, which in my view is where any disorder process in the monolayer starts.

3.1. Monolayers of Fatty Acids

Spontaneous adsorption of long chain *n*-alkanoic acids has been studied in the last few years. Allara and Nuzzo [31, 32] and Ogawa *et al.* [33] studied the adsorption of *n*-alkanoic acids on aluminum oxide, while Schlotter *et al.* studied the spontaneous adsorption of such acids on silver [34]. Huang and Tao studied

membrane layer is formed using elements having atomic numbers less than approximately 20.

A scattering layer is formed overlying the membrane layer 104. Typically, the scattering layer is formed using elements having an atomic number greater than approximately 72, such as tungsten, titanium, tantalum, tungsten silicide, titanium silicide, tantalum silicide, gold, and the like. The scattering layer is patterned and etched using a conventional etch process to form the scattering elements 108, as illustrated in FIG. 1. The bottom layer 100 is patterned and etched using a conventional nitride etch process to form an opening 103 in bottom layer 100. Portions of the substrate 102 are then removed to define a window portion 109. Functional portions of a representative SCAI.PEL mask are illustrated by the structure shown in FIG. 1.

In accordance with an embodiment of the present invention, FIG. 2 further illustrates the mask in FIG. 1, and now includes a self-assembled monolayer (SAM) 220 formed overlying the patterned scattering layer 108 and the membrane layer 104. The term monolayer herein refers to a film having an thickness approximately equal to a length of a single atom or molecule. The SAM 220 is typically a thin 1-5 nanometer organic layer that is adsorbed onto the surfaces of the membrane layer 104 and scattering layer 108. It generally has a structure that includes three portions, (1) a surface active head group that interacts with the surface of the mask, (2) an intermediate group that forms the chain of the molecule, and (3) an air-monolayer interface group that stabilizes the SAM 220.

SAM formation results from a molecular-substrate interaction in which the head group of the molecule is pinned to specific sites on the substrate surface via a chemical bond. In the case of a alkyltrichlorosilanes on hydroxylated or oxidized surfaces, a covalent Si—O bond is formed. After the molecules have been put in place on the surface of the substrate, the formation of orderly and closely packed alkyl chains begins, which is the intermediate portion of the molecule. The Van der Waals interactions between the alkyl chains are the main attractive forces in the case of the intermediate portions of the molecule. The third molecular component is the terminal functionality, which in the case of a simple alkyl chain is a methyl (CH₃) group.

In accordance with embodiments of the present invention, the entire surface of the mask is coated with a SAM. This may be accomplished in the presence of a native or a thermally grown oxide so as to provide appropriate nucleation sites for the SAM. In one embodiment, the outermost surface of the mask has an oxide component, either a native oxide or a purposely formed oxide, such as a thermal oxide or the like. Accordingly, the membrane layer 104, which is formed of silicon nitride, has a thin outer layer of silicon dioxide, and the scattering layer 108, which is formed of tantalum, has a thin outer layer of tantalum oxide. As noted above, the scattering layer may be formed of other materials, such as tantalum, tantalum silicide, tungsten, tungsten silicide, etc. The oxide layers are in a range of approximately 1-4 nanometers thick and provide an appropriate interface to which the SAM 220 adsorbs.

In one embodiment, the surface active head group of the SAM 220 is an organosilicon derivative. Additionally, the surface active head group of the SAM 220 may be any molecule that has been shown to self-assemble into a monolayer on a surface, including organic carboxylic and hydroxamic acids, organosulfur materials, organoselenium materials, alkyl materials, organophosphate materials, organoamine materials, organo-germanium materials, organosul-

phonate materials, and the like. Within the group of organosilicon derivatives, alkylchlorosilanes, alkylalkoxysilanes, alkylaminosilanes, and the like may be used to form self-assembled monolayers on the mask.

In a typical procedure, the substrate is placed into a solution of 10 (mM) millimolar octadecyltrichlorosilane (ODT) at room temperature (20° C.) for 1.5 hours (The 10 mM solution of ODT is prepared by dissolving 0.39 milliliter of ODT in 100 milliliter of an anhydrous aprotic solvent, such as hexadecane, immediately prior to use). After approximately 1.5 hours, the substrate is rinsed with hexane, ethanol, distilled water, and finally dried in a stream of nitrogen. During adsorption, the silicon component of the octadecyltrichlorosilane reacts with the oxidized surface to form a network of Si—O—Si bonds. The result is a self-assembled monolayer (SAM) in which the molecules are connected both to each other and to the substrate surface by chemical bonds.

FIG. 2 includes an illustration of the previously described self-assembled monolayer (SAM) 220 overlying the membrane 104 and the scattering layer 108. The self-assembled monolayer 220 is formed using a spin-on technique. Alternatively, the SAM 220 may be formed using an immersion, a solution deposition, a vapor deposition, or a micro-contact printing technique. The SAM is formed overlying the mask such that the transmission of the electron beam (e.g., 75-150 KeV) through the mask is relatively unobstructed. This is accomplished using self-assembled monolayers having low atomic number elements (less than approximately 20), such as silicon, carbon, oxygen, and the like, and thicknesses of less than approximately 10 nanometers. Typically, the thickness of the SAM is in a range of approximately 1.5-6.0 nanometers. In accordance with embodiments of the present invention, the SAM 220 is formed of a material that has an electron scattering power that is less than that of the scattering layer 108, due to differences in the atomic weight of the respective materials. The SAM 220 also has an electron scattering power that may be the same or different than that of the membrane layer 104.

FIG. 3 illustrates the embodiment shown in FIG. 2, after repeated use, such that defects 325 (particles) are present on the mask. As previously discussed, these defects are highly undesirable and should be removed. According to embodiments of the present invention, the defects 325 may be removed using various techniques. In one embodiment, the particles are removed from the SAM 220 using a dry cleaning process that leaves the SAM 220 intact. Examples of these include a dry laser cleaning process, a frozen ice cleaning process, or the like. In this embodiment, dry cleaning effectively removes the defects 325 because there is a weaker attractive force or bond between the defects 325 and the SAM 220 or between the terminal and intermediate portions of the SAM, as compared to the force of attraction that would otherwise be present between the defects 325 and the membrane 108 (i.e., an unprotected mask). As an additional benefit, the SAM 220 may be a buffer layer during cleaning and thus prevent damage to the scattering layer 108 and the membrane 104.

The SAM 220 may not always present on the mask while the mask is being used to expose the substrate. In some cases, it may be desirable to remove the particles 325 and the SAM 220 prior to using the mask. The removal can be done using either a plasma, a wet chemical, or a thermal process. In the case of a plasma process, an oxygen-containing plasma is used to remove the SAM 220. In the case of a wet chemical processes, an acidic solution may be used to dissolve the SAM 220. For example, in the case of the

ELECTRONIC DEVICES WITH COMPOSITE ATOMIC BARRIER FILM AND PROCESS FOR MAKING SAME

STATEMENT OF GOVERNMENT INTEREST

The invention described herein may be manufactured and used by or for the Government of the United States of America for Governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

This invention relates generally to the fabrication of electronic devices, and particularly to a novel barrier film for electronic and electro-optic materials.

Integrated circuits (ICs) are composed of many millions (sometimes billions) of components such as transistors, resistors, and capacitors. These individual components are laid out in a two dimensional array on a substrate such as silicon or gallium arsenide. The two dimensional arrays are often stacked one on top of another to form a three dimensional IC. As in any circuit, these components, and the several layers, must be connected to one another electrically. Interconnection on the two dimensional surfaces is accomplished by depositing strips of metal that act as connecting "wires." Likewise, the layers are interconnected by metal plugs deposited in via holes made between layers. These steps in the manufacturing process are commonly referred to as "metallization."

Generally, silicon is the substrate material of choice, aluminum is the metal of choice for two dimensional IC metallization, and tungsten is the metal of choice for filling via holes for multiple layer interconnection. Silicon is preferred because it is cheap and abundant. Aluminum and tungsten are chosen because they have adequate electrical conductivity and they can be made not to diffuse into the substrate during the many annealing operations inherent in the IC manufacturing process.

Because the electrical conductivity of aluminum and tungsten is limited, the "wires" and plugs must be made thick enough to ensure minimal resistance to electric current between components and between layers. The large size of these conductors has recently become an issue for IC designers and fabricators interested in placing a greater density of circuit elements on an IC. In order to achieve greater performance from ICs, the lateral dimensions of the circuit elements must be reduced. This reduction in IC element size has two detrimental effects on the resulting IC. First, it increases the resistance of the metal interconnects. Second, it increases the aspect ratio of the via holes, making them more difficult to fill with the metallic material. Incomplete filling of the via holes exacerbates the problem of high resistance. Today, there is often not enough space in the lateral direction on an IC chip to accommodate large aluminum conductors. Additionally, the size of the via holes, when filled with tungsten, limits the number of levels in the IC to no more than five.

Copper, which is a much better conductor of electricity than aluminum, is available as an alternative metallization material. Because of copper's greater electrical conductivity, copper imposes less resistance to the flow of electrons than aluminum or tungsten conductors having equivalent dimensions. The increasing density of components on today's ICs requires the smaller sized conductors that are only achievable by the use of highly conductive metallization materials.

Unfortunately, copper has one notable problem. It has a tendency to diffuse into silicon at elevated temperatures.

This has precluded copper as a metallization candidate because ICs must be annealed several times during the manufacturing process. In order for copper metallization to be feasible, a technique must be developed that will prevent the diffusion of copper into silicon. Among the possible solutions currently under development within the semiconductor industry the most prevalent is the use of nitrides of the transition metals titanium and tungsten. The thickness of the metal-nitride layer required to stop copper diffusion into silicon effectively is in the range of tens to hundreds of nanometers, or hundreds to thousands of Angstroms (Å).

The problem of diffusion exists not only in the case of copper metallization on silicon, but also in the case of copper metallization on other single- and polycrystalline semiconductor substrate materials such as gallium arsenide, silicon carbide, germanium, and so forth. Copper diffusion into insulating materials such as SiO₂ can also result in short circuits, especially in dense arrays of IC components. Diffusion is also a problem with other high conductivity metallization materials such as gold, silver, and platinum.

An object of this invention is to provide a barrier film which is extremely thin, yet permits metallization using copper and other high conductivity metallic conductors which would otherwise have a tendency to diffuse into a substrate formed of a semiconducting or insulating material.

It is also an object of the invention to improve electronic and electro-optic devices by making it possible to achieve one or more of the following desirable characteristics: increased component density in large scale integration, reduced heat dissipation, increased speed of operation, and a decreased number of layers.

Still another object is to provide a procedure for forming an extremely thin diffusion barrier, which produces consistent results rapidly and reliably, and which is not highly dependent upon the accurate maintenance of operating conditions such as time and temperature.

Still another object is to provide a process for forming an extremely thin diffusion barrier which eliminates voids and mechanical stresses that can have detrimental effects on the substrate, the diffusion barrier, or the metallization layer.

SUMMARY OF THE INVENTION

In accordance with this invention, a semiconductor device is fabricated by forming, on a surface of a substrate material, a barrier film having a monolayer of metal atoms immediately adjacent the surface of the substrate material. In one aspect, a metallic conductor, which has a tendency to diffuse into the substrate material, is then deposited onto the barrier film. Metallic conductors which have a tendency to diffuse into substrates of semiconductor or insulating materials include, for example, pure copper, copper alloys (e.g., Cu—Al, Cu—Si—Al), copper doped with a dopant (e.g., aluminum) that impedes electromigration, gold, silver, or platinum. For purposes of this invention, a "monolayer" is understood to refer to a two-dimensional array of atoms having the thickness of one atomic layer; although the monolayer may have minuscule defects such as minute portions with a thickness that exceeds one atomic layer and/or minute portions that are voids, the average thickness nonetheless essentially is an atomic layer providing essentially complete coverage of the directly underlying substrate surface regions. The monolayer, which is extremely thin by definition, serves as a barrier film, inhibiting diffusion of the metallic conductor into the substrate material. For purposes of this application, the material upon which the monolayer of atoms is formed is often generally referred to herein as a

electron pairs readily available for simultaneous donation to a metal ion coordinated by the chelating agent.

The term "biological binding" refers to the interaction between a corresponding pair of molecules that exhibit mutual affinity or binding capacity, typically specific or non-specific binding or interaction, including biochemical, physiological, and/or pharmaceutical interactions. Biological binding defines a type of interaction that occurs between pairs of molecules including proteins, nucleic acids, glycoproteins, carbohydrates, hormones and the like. Specific examples include antibody/antigen, antibody/hapten, enzyme/substrate, enzyme/inhibitor, enzyme/cofactor, binding protein/substrate, carrier protein/substrate, lectin/carbohydrate, receptor/hormone, receptor/effector, complementary strands of nucleic acid, protein/nucleic acid repressor/inducer, ligand/cell surface receptor, virus/ligand, etc.

The term "binding partner" refers to a molecule that can undergo biological binding with a particular biological molecule. For example, Protein A is a binding partner of the biological molecule IgG, and vice versa.

The term "biological molecule" refers to a molecule that can undergo biological binding with a particular biological binding partner.

The term "recognition region" refers to an area of a binding partner that recognizes a corresponding biological molecule and that facilitates biological binding with the molecule, and also refers to the corresponding region on the biological molecule. Recognition regions are typified by sequences of amino acids, molecular domains that promote van der Waals interactions, areas of corresponding molecules that interact physically as a molecular "lock and key", and the like.

The term "biologically inert", when describing the relationship between two species means that the two species do not undergo biological binding.

The term "coordination site" refers to a point on a metal ion that can accept an electron pair donated, for example, by a chelating agent.

The term "free coordination site" refers to a coordination site on a metal ion that is occupied by a water molecule or other species that is weakly donating relative to a polyamino acid tag, such as a histidine tag.

The term "coordination number" refers to the number of coordination sites on a metal ion that are available for accepting an electron pair.

The term "coordinate bond" refers to an interaction between an electron pair donor and a coordination site on a metal ion leading to an attractive force between the electron pair donor and the metal ion.

The term "coordination" refers to an interaction in which one multi-electron pair donor, such as a chelating agent or a polyamino acid tag acting as a chelating agent, coordinatively bonds (is "coordinated") to one metal ion with a degree of stability great enough that an interaction that relies upon such coordination for detection can be determined by a biosensor. The metal ion is coordinated by the multi-electron pair donor.

The term "solid phase" refers to any material insoluble in a medium containing a target molecule or biological molecule that is desirably captured in accordance with the invention. This term can refer to a metal film, optionally provided on a substrate.

The term "surface" refers to the outermost accessible molecular domain of a solid phase.

The term "capturing" refers to the analysis, recovery, detection, or other qualitative or quantitative determination

of an analyte in a particular medium. The medium is generally fluid, typically aqueous. The term, "captured", refers to a state of being removed from a medium onto a surface.

The term "target molecule" refers to a molecule, present in a medium, which is the object of attempted capture.

The term "determining" refers to quantitative or qualitative analysis of a species via, for example, spectroscopy, ellipsometry, piezoelectric measurement, immunoassay, and the like.

The term "immobilized", used with respect to a species, refers to a condition in which the species is attached to a surface with an attractive force stronger than attractive forces that are present in the intended environment of use of the surface and that act on the species, for example solvating and turbulent forces. Coordinate and covalent bonds are representative of attractive forces stronger than typical environmental forces. For example, a chelating agent immobilized at a surface, the surface being used to capture a biological molecule from a fluid medium, is attracted to the surface with a force stronger than forces acting on the chelating agent in the fluid medium, for example solvating and turbulent forces.

The term "non-specific binding" (NSB) refers to interaction between any species, present in a medium from which a target or biological molecule is desirably captured, and a binding partner or other species immobilized at a surface, other than desired biological binding between the biological molecule and the binding partner.

The term "self-assembled monolayer" refers to a relatively ordered assembly of molecules spontaneously chemisorbed on a surface, in which the molecules are oriented approximately parallel to each other and roughly perpendicular to the surface. Each of the molecules includes a functional group that adheres to the surface, and a portion that interacts with neighboring molecules in the monolayer to form the relatively ordered array. See Laibinis, P. E.; Hickman, J.; Wrighton, M. S.; Whitesides, G. M. *Science* 245, 845 (1989); Bain, C.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* 111, 7155-7164 (1989); Bain, C.; Whitesides, G. M. *J. Am. Chem. Soc.* 111, 7164-7175 (1989), each of which is incorporated herein by reference.

The term "self-assembled mixed monolayer" refers to a heterogeneous self-assembled monolayer, that is, one made up of a relatively ordered assembly of at least two different molecules.

The present invention provides a technique for molecular recognition at surfaces that involves electron transfer through a biological species immobilized at the surface. The surface presenting the immobilized biological species is exposed to a biological binding partner of the biological species, or a biological binding partner of a biological binding partner of the species, and electron transfer through the biological species and the biological binding partner determined.

In the case of many biological molecules, biological binding is extremely sensitive to orientation and conformation of the members involved in the binding, that is, the biological molecule and the binding partner. Accordingly, the manner of presentation of the binding partner at the surface to a medium containing the biological molecule is directly related to the sensitivity, and success, of the technique. The present invention presents a biological species such as a nucleic acid stand at the surface in a manner in which biological binding with the nucleic acid strand at the surface is facilitated (as described in the co-pending, commonly-owned applications both entitled "Molecular

back of any device. However, a judicious choice of the chemical medium may provide a material that would sustain a very large number of cycles. In addition, if the medium is kept at low temperatures (for example, in dry ice), side reactions are suppressed and fatigue may be minimized to a large extent; at low temperatures the persistence of the written form is extended considerably. Other molecules and matrices are possible candidates that could improve the speed, power consumption, and lifetime of the device.

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Orthogonal Self-Assembled Monolayers: Alkanethiols on Gold and Alkane Carboxylic Acids on Alumina

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This work demonstrates the practicality of forming two self-assembled monolayers (SAMs), independently but simultaneously, by adsorption of two different adsorbates from a common solution onto a substrate exposing two different materials at its surface. The experimental procedure and the degree of independence achieved in the resulting SAMs are illustrated by examination of monolayers obtained by adsorption of alkanethiols on gold and alkane carboxylic acids on alumina. This procedure provides a method for modifying the surface characteristics of microlithographically generated patterns and offers a versatile technique for controlling solid-vapor and solid-liquid interfacial properties in systems having patterns with dimensions of the order of 1 micrometer.

SELF-ASSEMBLED MONOLAYERS (SAMs) are highly ordered, quasi-two-dimensional structures formed by adsorption of appropriate precursors $X(CH_2)_nY$ from solution onto a solid substrate of metal or metal oxide (1-5). Techniques described to date for formation of SAMs offer very precise control over structure in the dimension perpendicular to the plane of the monolayer (2) but little control over structure or composition in the plane of the monolayer. For studies in wetting (3) and in microelectrochemistry (6, 7), we also wanted to be able to control structure and to form patterns in the plane of the monolayer. We describe a technique that combines the formation of SAMs with the microlithographic preparation of substrates for them having two or more materials exposed at their surface. This technique provides control over in-plane surface properties and structure at the scale of the dimensions reached

by the microlithographically generated features.

We take advantage of systems of adsorbants (A_1, A_2, \dots) and substrates (S_1, S_2, \dots) that are "orthogonal" in formation of SAMs: that is, A_i adsorbs strongly on S_i but weakly on S_j ; A_j adsorbs strongly on S_j but weakly on S_i . A number of orthogonal systems can be imagined based on different principles of surface coordination chemistry. In this report we illustrate the application of orthogonal systems to the formation of in-plane patterns using "hard" and "soft" acid-base interactions (8) to differentiate between areas in the plane: $S_1 = Al_2O_3$, $A_1 = RCO_2H$; and $S_2 = Au$, $A_2 = R'SH$.

To demonstrate orthogonality in SAMs formed on the different substrates, a number of preliminary experiments were conducted with areas large enough for contact angle and x-ray photoelectron spectroscopy (XPS) measurements. In these experiments, substrates were prepared by evaporation of aluminum (~500 Å) through a mask onto a gold substrate (9). On exposure of this patterned system to air, the surface of the aluminum oxidized spontaneously to aluminum oxide. Immersion of this substrate in an isooctane solution (10) containing an

alkanethiol, $HS(CH_2)_mX$, and an alkane carboxylic acid, $HO_2C(CH_2)_nY$ (each ~1 mM), for 24 hours resulted in adsorption of the thiol preferentially on the gold (4) and the carboxylic acid preferentially on the aluminum oxide (Fig. 1) (5). The composition of the SAMs formed on the gold and alumina were examined by XPS (11) (Fig. 2) and wettability (Table 1). The important conclusion from the data in Table 1 is that, within the limits of detection of our experiments, pure monolayers of the two adsorbates— $HS(CH_2)_mX$ on gold and $HO_2C(CH_2)_nY$ on alumina—are formed independently on the two types of exposed interfaces by ad-

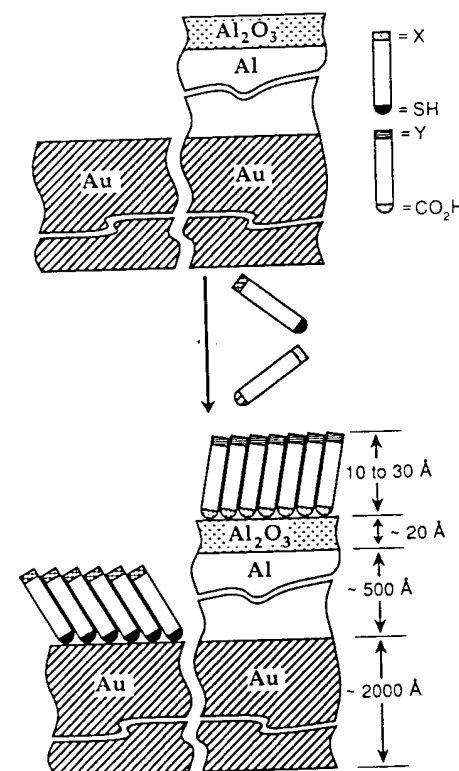


Fig. 1. Schematic illustration of the formation of orthogonal SAMs by adsorption of a mixture of alkanethiol $[HS(CH_2)_mX]$ and alkyl carboxylic acid $[HO_2C(CH_2)_nY]$ from a common solution onto a patterned gold-aluminum oxide surface.

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Table 1. Analysis of the organic monolayers formed by exposure of a substrate that has gold and alumina overlayers to a solution containing $\text{HS}(\text{CH}_2)_m\text{X}$ and $\text{HO}_2\text{C}(\text{CH}_2)_n\text{Y}$. We estimate the threshold of detection of an XPS tag on the orthogonal surface (such as X on Al_2O_3 or Y on Au) to be 2 to 3% by mole for Br, ~1% by mole for Cl, and <0.5% by mole for F. The wetting data are advancing contact angles of water.

HS(CH ₂) _m X		HO ₂ C(CH ₂) _n Y		Result
X	m	Y	n	
XPS				
CH ₃	17	Br	15	Br only on Al ₂ O ₃
Br	11	CH ₃	16	Br only on Au
CH ₃	17	Cl	15	Cl only on Al ₂ O ₃
Cl	11	CH ₃	16	Cl only on Au
CH ₃	17	NHCOCF ₃	11	F only on Al ₂ O ₃
OCH ₂ C ₂ F ₅	11	CH ₃	16	F only on Au
Wetting				
OH*	11	CH ₃	17	θ _A ^{Au} < 15°; θ _A ^{Al₂O₃} = 96°
CH ₃	17	OH	15	θ _A ^{Au} = 104°; θ _A ^{Al₂O₃} = 75°

*Adsorption for this system was performed with anhydrous ethanol as the solvent.

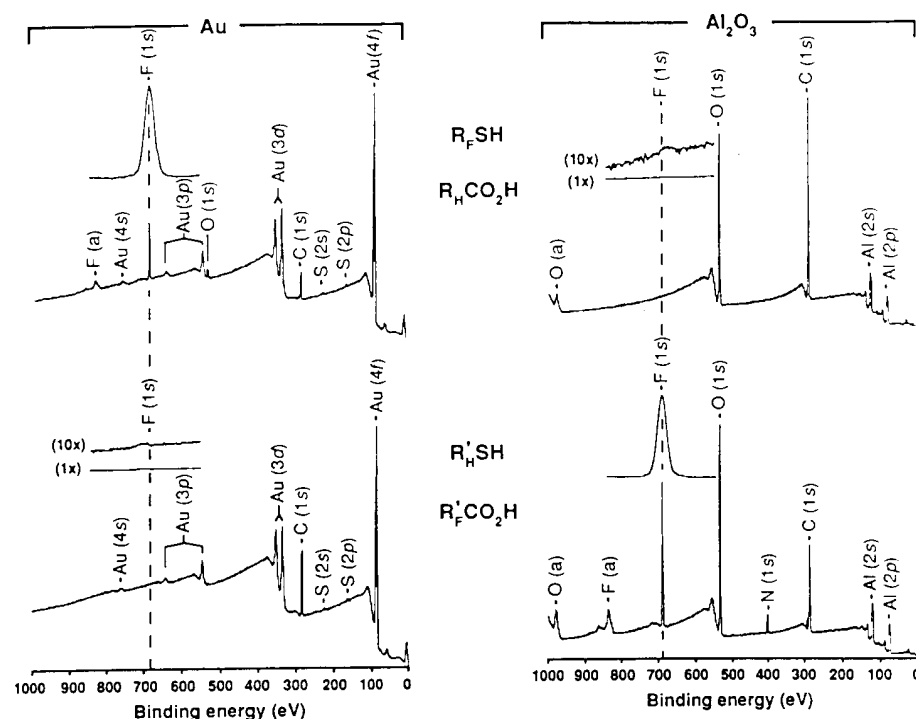


Fig. 2. XPS of SAMs formed from solutions containing mixtures of thiol and carboxylic acid on gold (left) and alumina (right); $\text{R}_\text{F}\text{SH} = \text{CF}_3\text{CF}_2\text{CH}_2\text{O}(\text{CH}_2)_{11}\text{SH}$, $\text{R}_\text{H}\text{CO}_2\text{H} = \text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$; and $\text{R}'_\text{F}\text{SH} = \text{CH}_3(\text{CH}_2)_{17}\text{SH}$, $\text{R}'_\text{F}\text{CO}_2\text{H} = \text{CF}_3\text{CONH}(\text{CH}_2)_{11}\text{CO}_2\text{H}$. Each sample is represented by a survey spectrum and by an insert showing the $\text{F}(1s)$ region scanned from 680 to 700 eV at high resolution.

sorption from the same isooctane solution. Figure 2 shows XPS data for the system in which the sensitivity of XPS analysis is the highest (that based on detection of fluorine). The high degree of discrimination is clearly evident from the high-resolution spectra of the $\text{F}(1s)$ region. The selectivity for binding is at least 100 to 1.

To demonstrate the formation of orthogonal SAMs at dimensions of greater interest in studying wetting and microelectrochemistry ($\leq 1 \mu\text{m}$), microelectrode arrays (7)

were prepared on an insulating silicon nitride surface comprising eight wires—four gold and four aluminum. Each wire was $\sim 2.4 \mu\text{m}$ wide, $\sim 100 \mu\text{m}$ long, and $\sim 1000 \text{ \AA}$ thick; the wires were separated by 1 to 2 μm . The array was cleaned by 30-min periods of sonication in sequence in hexanes, CH_2Cl_2 and CH_3OH , and was then exposed for 1 min to a flowing O_2 plasma (0.3 torr). The SAMs were formed by exposing the clean grid to a mixture of $\text{CF}_3(\text{CF}_2)_8\text{CO}_2\text{H}$ and $\text{Cl}(\text{CH}_2)_{11}\text{SH}$, each

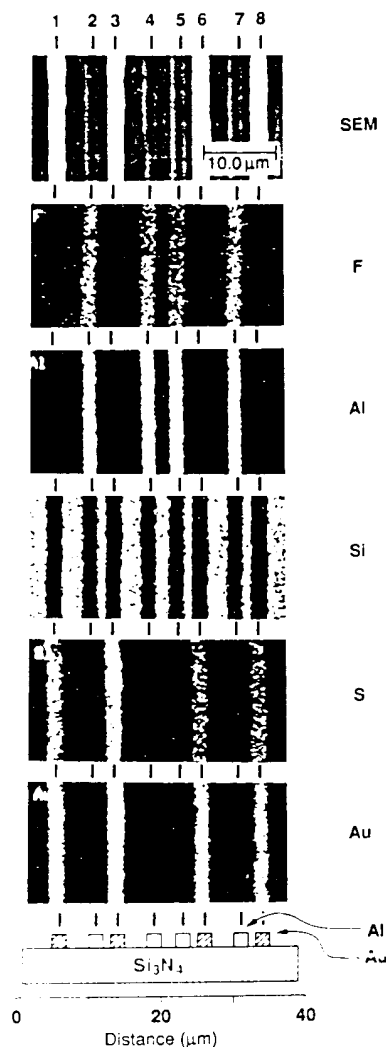


Fig. 3. Scanning electron micrographs (SEM) and scanning Auger element maps for an array of four strips of gold (numbers 1, 3, 6, and 8) and four of aluminum/alumina (numbers 2, 4, 5, and 7) on a silicon nitride (Si_3N_4) substrate. The SAM on gold is of $\text{HS}(\text{CH}_2)_{11}\text{Cl}$; that on alumina is of $\text{CF}_3(\text{CF}_2)_8\text{CO}_2\text{H}$. The schematic illustration of the device is a side view; the Auger element maps and the SEM are top views.

$\sim 1 \mu\text{M}$, in isooctane (10) for 24 hours, which was then removed from solution and washed with hexanes. The device was grounded to a stage with silver paint and introduced into a scanning Auger microprobe spectrometer (12). Figure 3 shows a scanning electron micrograph and Auger element maps of the array. Beam damage to the derivatized array prohibited individual mapping of both halogen tags; sulfur, which proved to be less labile than chlorine, was mapped instead of chlorine. The maps establish that the fluorine is localized on the alumina, the sulfur on the gold, and that neither adsorbent is present on the silicon nitride. The selectivity inferred in these experiments is also at least 100 to 1.

The entries in Table 1 demonstrate the formation of several representative orthogo-

SAMs. A large number of different organic functionalities should be compatible with this procedure. The last entry for Table illustrates, however, one important current limitation of the technique. Although either hydrophobic or hydrophilic SAMs can be formed on gold, only hydrophobic SAMs can presently be formed on alumina: molecules $X(CH_2)_nY$ in which both X and Y are hydrophilic appear to adsorb with both polar functionalities bound at the alumina surface, and thus appear to form looped structures that are hydrophobic. This phenomenon occurs not only with alumina but seems to be common to metal oxides.

The technique of simultaneous formation of two different SAMs on a common, microtopographically prepared substrate exposing patterns of two different materials provides a new method for controlling and modifying the characteristics of surfaces. Since SAMs afford a high degree of control at the 2 Å scale perpendicular to the plane of the monolayer, and since lithography provides the ability to form lateral features having dimensions as small as 50 Å (13), the combination of the two offers a highly versatile protocol for the control of surface structure and properties.

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- The gold substrate was prepared by evaporation of 100 Å of 99.99% chromium onto a polished Si(111) wafer followed by 2000 Å of 99.999% gold with the use of a cryogenically pumped E-beam evaporator operating at 10^{-6} torr.
- For adsorbates only partially soluble in isooctane, substitution of anhydrous ethanol for isooctane yielded similar XPS and Auger results.
- XPS spectra were obtained on a Surface Science Instruments spectrometer (Model SSX-100) operated at $<3 \times 10^{-9}$ torr with a 1-mm spot size.
- Auger analysis was performed using a PHI 660 scanning Auger spectrometer operating at $<2 \times 10^{-9}$ torr. Mapping of SAMs proved to be extremely difficult at normal beam parameters. Although beam damage was minimized by using very low beam energies (0.5 to 3 nA, 8 to 15 kV), damage to some SAMs was so significant that element maps could only be obtained on the first pass.
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Evidence from Sediments of Long-Term *Acanthaster planci* Predation on Corals of the Great Barrier Reef

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Since 1962 the crown-of-thorns starfish, *Acanthaster planci*, has caused the devastation of living coral in large tracts of the Great Barrier Reef, Australia. Some authorities view this as a modern phenomenon, resulting from ecological disturbance caused by man. Evidence from skeletal remains in sediment suggests that large *A. planci* populations have been part of the Great Barrier Reef ecosystem for at least 8000 years. Coral predation by *A. planci* is likely to have influenced the morphological fabric of the Great Barrier Reef in its post-glacial development and may also have influenced species richness of the reef biota.

THE CROWN-OF-THORNS STARFISH (*Acanthaster planci* L.) is a major predator of hermatypic scleractinian corals, particularly in the western Pacific region (1, 2). Its population dynamics are considered to be cyclic (3) with low population densities alternating with dramatic population outbreaks that result in massive damage to the living coral cover of individual reefs and reef tracts (4, 5). The Great Barrier Reef has experienced two documented contemporary cycles, with outbreaks affecting reefs between Princess Charlotte Bay and the Swain Reefs Complex in the periods 1962 to 1977 and 1979 to 1986 (6, 7). It is thought that outbreaks occur first in the Cairns section of the Great Barrier Reef with reefs further south becoming progressively infested (6). Extensive regional surveys undertaken during 1985–86 indicated that, of 228 reefs surveyed in the Great Barrier Reef Province, approximately 27% had been affected by *A. planci* in the outbreaks of the present cycle (7).

The temporal context of the present crown-of-thorns predation cycles is a contentious issue. Some investigators argue that the cycles are a contemporary phenomenon directly attributable to interference by man in reefal ecosystems (8) thereby raising a major conservation issue in Australia and elsewhere. A converse view is that crown-of-

thorn outbreaks represent an enduring ecological pattern that escaped notice until recently (9). The antiquity of *A. planci* outbreaks in the Great Barrier Reef is an important question to be answered.

Acanthaster planci contains a complex skeleton of small, arm-supporting ossicles and protective spines made of calcite. After death, these skeletal elements accumulate with reef sand as a recoverable fossil record. They are distinctive in color, shape, and microtexture and can be distinguished with certainty from other carbonate grains (10). Although the potential of this record in assessing the temporal distribution of *A.*

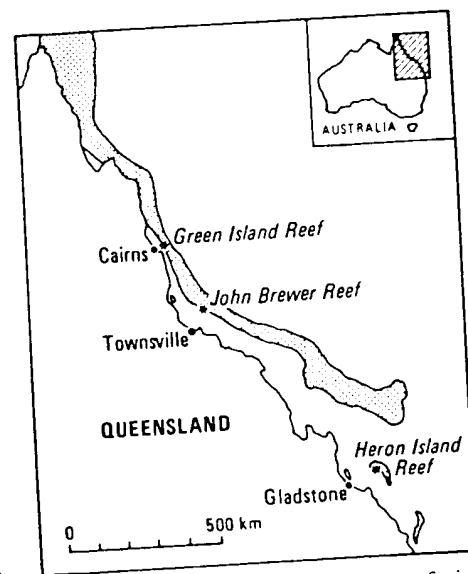


Fig. 1. Location of Great Barrier Reef sites examined for *A. planci* skeletal elements in the sediment record.

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